Development of low-temperature thick-film materials for piezoresistive sensors

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Abstract

Thick-film materials are very advantageous for piezoresistive pressure and force sensors because of ease of processing, reliability and low cost. However, their applications are restricted because standard thick-film materials require processing temperatures around 850°C, which essentially restricts them to ceramic substrates.
In this work, we examine the processing and properties of thick-film dielectric and resistor compositions designed to sinter at lower temperatures, making them compatible with high-strength stainless steel alloys (<700°C). Both dielectric and resistor materials are based on a lead borosilicate glass matrix, with suitable filler materials such as SiO_2 (quartz) and Al_2O_3 for the dielectrics and RuO_2 for the resistor. The materials were investigated X-ray diffraction, mechanical and electrical testing.
During firing, the thick-film materials undergo liquid-phase sintering through the glass matrix. Glass-filler chemical interactions are significant in the case of SiO_2 filler, and very small with Al_2O_3 or RuO_2. By adjusting the fillers, the glass composition and the processing parameters, we can obtain suitable thick-film materials for piezoresistive sensors with low processing temperatures, compatible with high-strength steel substrates.

1. Introduction

Thick-film technology applied to piezoresistive force or pressure sensing typically uses alumina as a substrate material, because it is the standard for thick-film technology [1]. However, alumina is not optimal for piezoresistive sensing applications, as its elastic modulus is high and its strength rather low [2]. Additionally, alumina is brittle and therefore ill suited to harsh environments and its heat dissipation capabilities are limited. Stainless steels [3] offer advantages in applications such as high-range load cells, due to their excellent thermal dissipation, mechanical sturdiness and easy packaging. Metallic materials also offer advantages such as robustness and ease of fabrication.

However, the high temperatures associated with commercial thick-film processing (850°C) are not compatible with high-strength steel, owing to degradation of mechanical properties of steel due to annealing or dimensional changes associated with martensitic transformation (which tend to destroy the thick-film layers). Additionally, standard thick-film materials are thermally matched to alumina, which has a rather low TCE (thermal coefficient of expansion) of ca. 7 ppm/K, whereas steels range from 11 (ferritic or martensitic) to 17 ppm/K (austenitic). Appropriate low-temperature thick-film systems (dielectrics, resistors and conductors) are therefore necessary.

In this work, we endeavour to investigate novel low-temperature thick-film dielectrics, conductors and resistors and present the resulting electrical properties of the resistors, compared with standard alumina-based systems. Relevant parameters such as adhesion, dissolution of filler powder in the glass matrix, temperature coefficient of resistance (TCR) and piezoresistance, are studied and discussed.

2. Experimental

The following substrate materials were used: 96% pure alumina (Kyocera, Japan, A-476, TCE = 7 ppm/K) as standard thick film substrate, ferritic stainless steel 1.4016 (TCE = 11 ppm/K) and austenitic stainless steel 1.4435 (TCE = 17 ppm/K). The steels were chosen because they have representative chemical (surface oxide) and thermal expansion properties (ferritic: ca. 11 ppm/K; austenitic: ca. 17 ppm/K). The steels were pre-oxidised at 900°C during 1 hour in order to increase the adherence of the dielectrics. This oxidation was particularly necessary for the 1.4435 stainless steel.

Four thick film dielectric materials based on 2 lead borosilicate glasses (V6 and V8), loaded with different powder concentrations, were developed, evaluated, and compared with high temperature commercial dielectrics. The list is given in the Table 1. The filler powder (alumina or quartz) serves to dimensionally stabilise the dielectric, and to control its TCE.

	Glass matrix	%vol Alumina powder	%vol Quartz powder
V6A40	V6	40	
V6Q40	V6		40
V8A40	V8	40	
V8Q40	V8		40

Table 1: List of the studied dielectric compositions.

The average particle size is 1 μm for alumina powder and 3 μm for quartz powder. The composition (by mass) of the glasses is V6: 75% PbO + 10% B_2O_3 + 15% SiO_2, and V8: 85% PbO + 10% B_2O_3 + 5% SiO_2. In both cases, 2% Al_2O_3 was added to inhibit crystallisation [4]. The ideal firing temperature is around 600°C for V6-based materials and around 500°C for V8-based ones.

The above dielectrics have been compared with two commercial dielectric materials, which must be fired at 850°C: Electro Science Laboratories (ESL) 4924 and Heraeus (Her) GPA 98-029. An additional dielectric, ESL 4916, was used on steel as an interlayer to decrease interfacial stresses.

We therefore have three firing temperature ranges: high (850°C), intermediate (around 600°C) and low (around 500°C) for commercial, V6-based and V8-based dielectrics respectively. To complete each materials system, adapted conductor and resistor materials were applied (Table 2).

For the high temperature range, standard ESL 9635B (Ag:Pd 3:1 conductor) and DuPont (Du) 2041 (10 kOhm standard resistor) were applied. For the intermediate one, we used ESL 9912 (Ag, fired at the same temperature as the underlying dielectric) and ESL 3114 (10 kOhm, 625°C firing for porcelain enamelled steel). Last, the low temperature materials were a 3:1 (vol.) mix of ESL 9912 with V8 (used as a frit in an attempt to improve the chemical compatibility between conductor and resistor materials), and an experimental resistive composition consisting of V8 glass loaded with 7.5% Vol. 400 nm RuO_2 nano-powder [5].

In all cases, the firing cycle started with a 15 min dwell at 370°C for organic burnout, followed by a 20 min dwell time at the indicated temperature. For each sample, three layers of dielectrics were screen-printed and fired according to the abovementioned cycle on each substrate in order to guarantee good insulation (40μm). The conductors were fired as indicated in Table 2.

Substrates	**Dielectrics**	**Conductor**	**Resistor**
Alumina, 1.4016, 1.4435	Commercial 850°C	ESL9635B 850°C	Du2041 850°C
1.4016, 1.4435	V6-based 575…625°C	ESL9912 575…625°C	ESL3114 625°C
1.4016, 1.4435	V8-based 500…550°C	ESL9912 : V8 500°C	0.075-400-8 500°C

Table 2: List of sample series and firing temperatures.

Samples for sheet resistance (SR) and TCR were 1.5 mm wide resistors of several lengths (Figure 1). Sheet resistance and TCR were measured as a function of resistor length at 30°C and 100°C. Gauge factor (GF) was determined at RT (23…26°C) by applying appropriate loads at the end of test cantilevers (Figure 2).

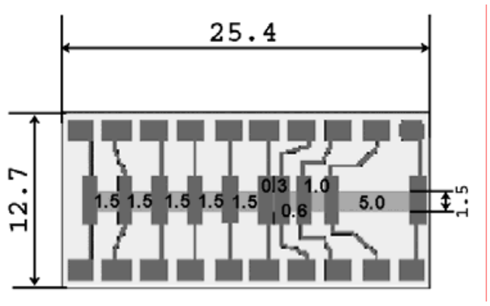

Figure 1: Layout of the test samples for SR and TCR measurements.

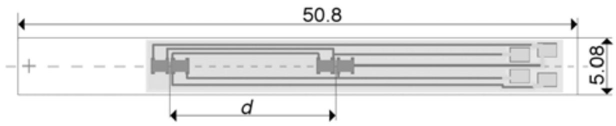

Figure 2: Layout of samples for piezoresistive measurement (depicted here: longitudinal).

3. X-Ray diffraction – dissolution of quartz

The dissolution temperature of quartz filler in the V8 and V6 glass was evaluated by XRD (Figure 3). For fillers (10% volume), dissolution of powders in V6 and V8 glasses occurs around 625°C and 600°C respectively.

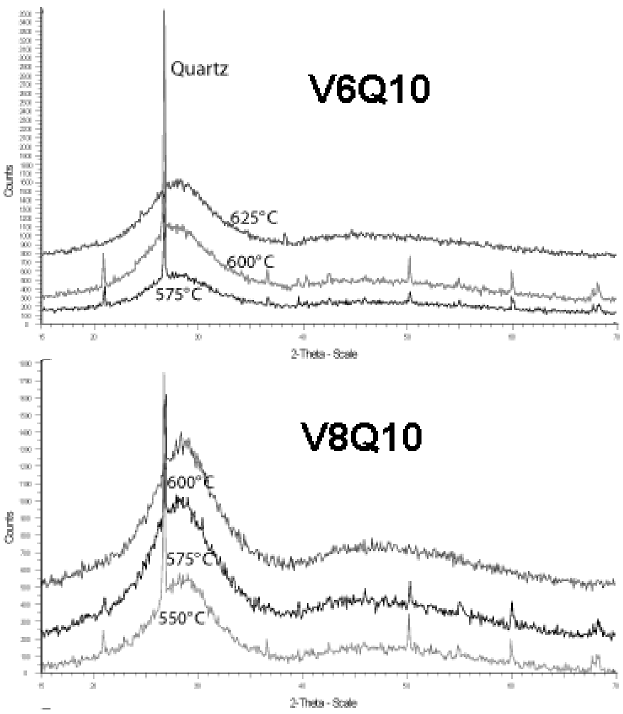

Figure 3:X-Ray diffraction of dielectrics based on V8 and V6 filled at 10% vol. with quartz.

4. Electrical properties and gauge factors

4.1 Low-temperature system

For this study, most of 1.4016 stainless steel substrates have been oxidised 1 hour at 900°C in order to create an oxide layer on the substrate surface, thereby improving the adherence of the dielectric thick-film on the steel. This study has been carried out on both oxidised and non oxidised substrates, with the conductor and resistor fired at 500°C. Figure 4 and Table 3 show the resulting sheet resistance, TCR and GF values. For this temperature range, the steel pre-treatment has no significant effect on the resistor properties.

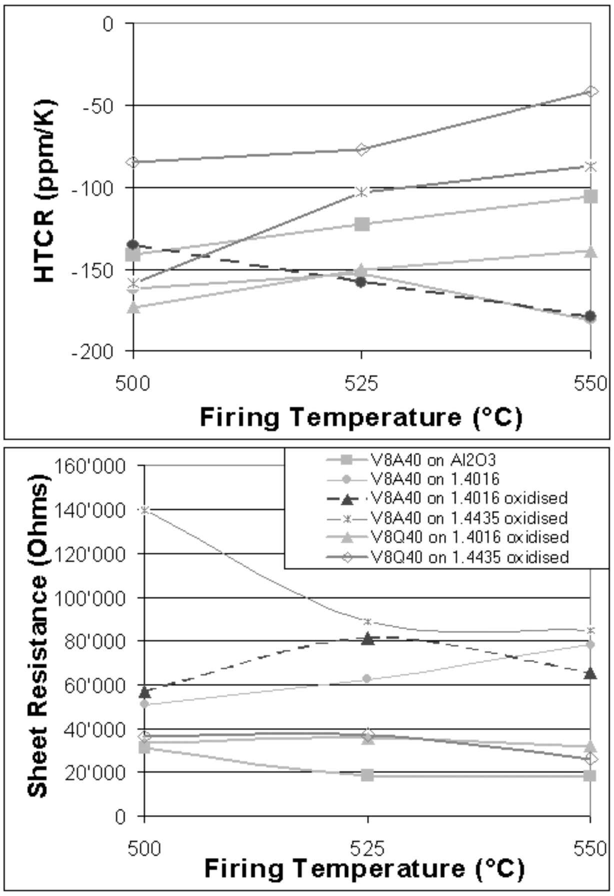

Figure 4: TCR and sheet resistance of 0.075-400-8 resistor for low-firing system.

Underlayer	Alumina		1.4016		1.4435	
	L	T	L	T	L	T
(alumina)	6.4	6.4 6.2	-	-	-	-
V8A40-525	-	-	5.0	5.7	7.3	-
V8Q40-500	-	-	6.7	4.8	7.9	5.3
V8Q40-525	-	-	6.0	5.2	6.5	5.0
V8Q40-550	-	-	6.1	4.4	6.1	5.3

Table 3: Gauge factor of 0.075-400-8 resistor for low-firing system. L = longitudinal; T = transverse.

Properties were found not to vary considerably with the dielectric firing temperature. Some of the steel samples were distorted by their manufacture (they were cut out of sheet). This gives rise to the observed high dispersion of SR and GF values. Additional distortion was imparted on 1.4435 by the alumina-filled dielectric due to poorer TCE matching, leading to some unreliability in the measurements.

TCR values on steel are tendencially higher (ca. 60 ppm/K) on 1.4435 than on 1.4016. The V8-based dielectrics are not suited for alumina, as their TCE is too high. This is also the case for the resistor: corresponding samples were rapidly measured after manufacture, as delayed cracking is observed at room temperature.

The GF of our experimental resistor is rather low, and must therefore be improved. Quartz is well adapted as a TCE controlling filler for this temperature range, as it is not dissolved significantly by the glass (see Figure 3).

4.2. Intermediate temperature system

The resulting properties for this series are shown in Figure 5 and Table 4. The V6A40 dielectric (alumina filler) has a strong influence on the value of the resistor, which is not the case of V6Q40 (quartz). Gauge factors (only T samples could be measured) were found to be significantly higher on both dielectrics than on alumina.

Excessive dissolution of the quartz by the glass at 625°C (resistor firing temperature) leads to dimensional instability of the thick-film circuit, which is also observed to a lesser extent on V6A40. Future work should therefore use lower firing resistors, as this would also improve compatibility with metal and glass substrates. Alternatively, the dimensional stability may be improved by increasing the filler concentration.

As for the V8 system, TCR is higher on 1.4435 than on 1.4016, and direct comparison with alumina is not possible due to excessive TCE of the dielectrics.

Underlayer	Alumina		1.4016		1.4435	
	L	T	L	T	L	T
(alumina)	10.5 11.3 11.1	8.2 9.0 8.6	-	-	-	-
V6A40-575	-	-	-	11.9	-	13.9
V6Q40-575	-	-	-	11.3	-	15.0
V6Q40-600	-	-	-	10.1	-	13.3
V6Q40-625	-	-	-	10.8	-	13.3

Table 4: Gauge factor of ESL 3114 (intermediate system). L = longitudinal; T = transverse.

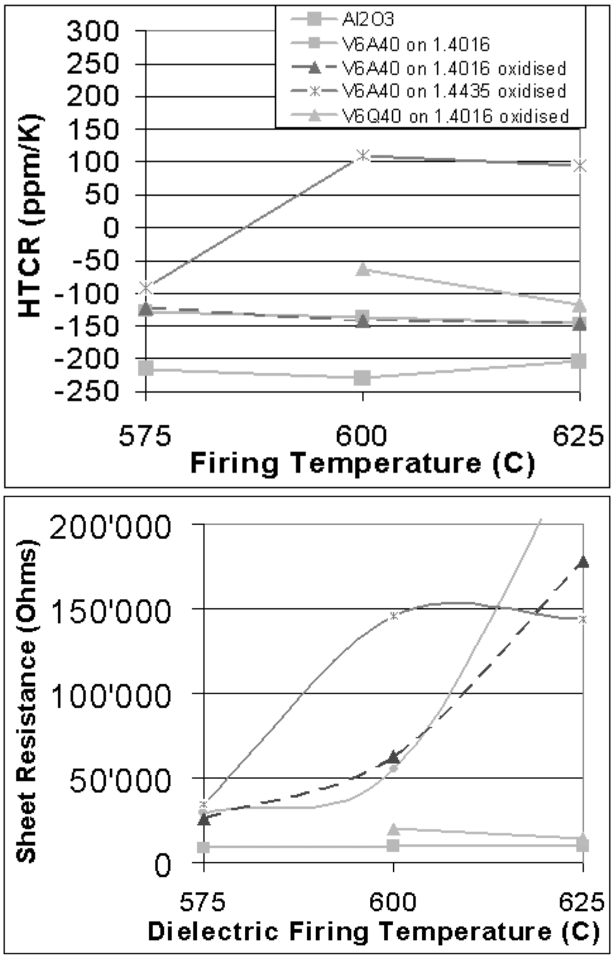

Figure 5: TCR and Sheet Resistance of ESL 3114 resistor on V6A40 dielectric as function of dielectric firing temperature.

4.3. High temperature system

For this study, the austenitic steel samples were pre-oxidised in order to improve the adherence of the dielectrics. Results are given in Figure 6 and Table 5.

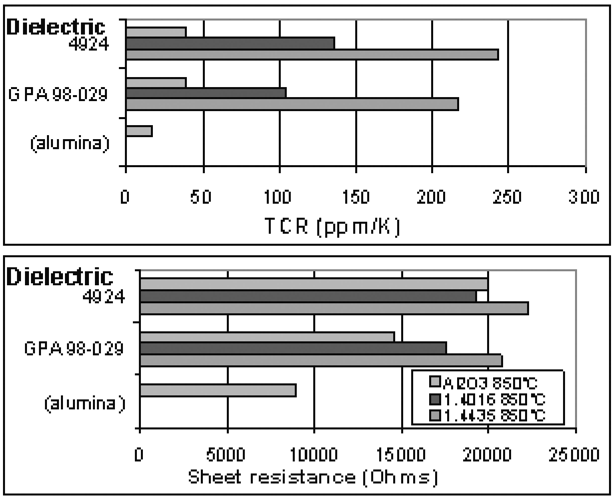

Figure 6: SR and TCR of Du 2041 Resistor on commercial dielectrics.

Underlayer	Alumina		1.4016		1.4435	
	L	T	L	T	L	T
(alumina)	12.5	8.3	-	-	-	-
GPA 98-029	12.4	7.6	10.6	6.7	-	-
4924	-	6.8	9.9	6.0	12.2	-

Table 5: Gauge factor of Du 2041 resistor for high-firing system. L = longitudinal; T = transverse.

Good compatibility is obtained on all dielectrics: no strong influence is observed on the measured values. As resistor and dielectrics have a good TCE match to alumina, the resistor film may be compared on all substrates with the same underlayer (although compressive stresses on steel give rise to some distortion, especially on 1.4435). As for the low and intermediate-firing system, TCR increases in function of the substrate TCE, in accordance with previous results [6].

5. Conclusion and outlook

The study has characterised two thick-film materials systems with a lower firing temperature. These systems exhibit promising electrical and piezoresistive properties and therefore show potential for application in sensors and electronics on metal substrates and glass. Adapting the filler and glass allowed matching the TCE of the dielectric materials to that of the substrate reasonably well.
The dielectrics are however still lacking in dimensional stability upon firing of additional conductor and resistor layers. This topic will therefore be the object of future work.

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